Kinetics. The hydrolytic rate constants were measured in degassed 1:1 CH_3CN/H_2O containing 0.025 M potassium phosphate. The increase in OD at 400 nm was monitored for 10^{-4} M solutions of the *p*-nitrophenyl esters **1** with a Cary 14 spectrophotometer; for 10^{-3} M solutions of phenyl esters **2**, the increase at 290 nm was monitored. Pseudo-first-order rate constants, cited below, were obtained from a least-squares analysis of the data.

The kinetic data are given in the format substrate: rate constant in s^{-1} (pH). **1a**: 3.1×10^{-2} (13.1), 4.1×10^{-3} (12.3); **1b**: 4.9×10^{-2} (12.6), 6.9×10^{-3} (11.7); **1c**: 2.2×10^{-2} (11.4), 7.3×10^{-3} (10.8); **1d**: 0.13 (11.6), 2.4×10^{-3} (10.0); **1e**: 47 (12.76), 12.2 (11.85), 0.79 (10.65); **1f**: 7.1 (12.8), 3.8 (11.9), 1.1 (11.0); **2a**: 6.5×10^{-4} (13.3); **2b**: 1.8×10^{-3} (13.4), 8.9×10^{-4} (13.0); **2c**: 2.5×10^{-3} (13.15), 5.0×10^{-4} (12.5); **2d**: 1.4×10^{-2} (13.4), 6.8×10^{-3} (13.0), 1.3×10^{-3} (12.4); **2e**: 1.0×10^{-3} (13.4), 4.5×10^{-4} (12.8); **2f**: 1.25×10^{-3} (13.2), 2.4×10^{-4} (12.5); **7**: 1.14×10^{-2} (13.3); **8**: 2.05×10^{-4} (13.3).

Hydrolysis of ^{18}O-Labeled 1c. A solution of 40 mg of **1c** in 1 mL of dry THF, containing 40 μL of 98% ^{18}O-enriched H_2O and one drop of trifluoroacetic acid, stood for 10 h at 25 °C. After removing the volatiles by mass spectrometry, the recovered **1c** contained 32% ^{18}O at C_3.

A solution of 20 mg of labeled **1c** in 2 mL of 1:1 CH_3CN/aqueous potassium phosphate buffer at pH 11 was stirred for 5 min, quenched with KH_2PO_4, and extracted with EtOAc. The crude extract was treated with a large excess of CH_2N_2 in Et_2O for 10 min and stripped to dryness to yield a 1:3 mixture of **4** and **1c**. (Methylation was required to prevent decarboxylation during mass spectral analysis.) Filtration of the crude residue through a silica gel pad with CH_2Cl_2 eluted a mixture of recovered labeled **1c** and **4**. The mixture was resolved by preparative thin-liquid chromatography (TLC) on silica gel with CH_2Cl_2. (The extent of exchange of the ^{18}O label from the ketone carbonyl was a function of how long the compound was on the TLC plate.) **4**: NMR 1.43 (s, 6 H), 3.68 (s, 3 H), 4.7 (s, 2 H), 6.9 (m, 3 H), 7.23 (m, 2 H).

Analysis of ^{18}O Distribution. Esters **4** and **1c**, upon electron impact in the mass spectrometer, generate the following set of ions: M^+, M - OR, M - CO_2R, M - OC_6H_5. The ^{18}O enrichment for each ion can be determined by comparison of the above peaks to their counterparts two mass units higher after correction for the natural isotopic distribution. The data are given in the format substrate, MS ion (% ^{18}O incorporation). Labeled **1c** prior to hydrolysis: M^+ (32), M - OC_6H_5 (32), M - CO_2Ar (32); **1c** recovered after partial hydrolysis prior to preparative TLC: M^+ (29), M - OC_6H_5 (30); **1c** recovered after H_3O^+ exchange: M^+ (0); **4** prior to preparative TLC: M^+ (30), M - OC_6H_5 (30); **4** after preparative TLC: M^+ (18), M - CO_2Me (8), M - OC_6H_5 (20); **4** after H_3O^+ exchange: M^+ (15), M - CO_2Me (0), M - OC_6H_5 (15).

Acknowledgment. We thank Joe Wright for the ^{18}O mass spectral analyses and Prof. William Jencks for many helpful discussions.

Registry No. 1a, 103439-27-6; **1b**, 103439-28-7; **1c**, 103439-29-8; **1c**-^{18}O, 103439-40-3; **1d**, 103439-30-1; **1e**, 103439-31-2; **1e**-^{18}O, 103439-42-5; **1f**, 103439-32-3; **1g**, 103439-33-4; **2a**, 103439-34-5; **2b**, 103439-35-6; **2c**, 103439-36-7; **2d**, 103439-37-8; **2e**, 103439-38-9; **2f**, 103439-39-0; **4**, 103439-41-4; $CH_3C(O)Cl$, 75-36-5; $CH_3OCH_2C(O)Cl$, 38870-89-2; $PhOCH_2C(O)Cl$, 701-99-5; $CH_2ClC(O)Cl$, 79-04-9; $CHF_2C(O)Cl$, 381-72-6; $CF_3C(O)Cl$, 354-32-5; $CCl_3C(O)Cl$, 76-02-8; $CH_3C(O)C(CH_3)_2C(O)Cl$, 30274-05-6; $CH_3OCH_2C(O)C(CH_3)_2C(O)Cl$, 103439-23-2; $PhOCH_2C(O)C(CH_3)_2C(O)Cl$, 103439-24-3; $CH_2ClC(O)C(CH_3)_2C(O)Cl$, 30274-02-3; $CHF_2C(O)C(CH_3)_2C(O)Cl$, 103439-25-4; $CF_3C(O)C(CH_3)_2C(O)Cl$, 103439-26-5; $CCl_3C(O)C(CH_3)_2C(O)Cl$, 17953-83-2; *p*-$NO_2C_6H_4OH$, 100-02-7; *p*-$NO_2C_6H_4{}^{18}OH$, 20168-37-0; PhOH, 108-95-2; dimethylketene, 598-26-5.

Lewis Acid Catalysis of Photochemical Reactions. 6. Selective Isomerization of β-Furylacrylic and Urocanic Esters

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Abstract: The spectroscopic properties and thermal and photochemical isomerization reactions of (*E*)- and (*Z*)-β-furylacrylic and urocanic esters in the presence and absence of Lewis acids have been investigated. As is the case for cinnamic esters, complexation of β-furacrylic esters occurs on the carbonyl oxygen and results in a large red shift in the electronic absorption spectra and photostationary states enriched in the thermodynamically less stable *Z* isomer. Unlike cinnamic and β-furlacrylic esters, the *Z* isomer of methyl urocanate is more stable than the *E* isomer due to the formation of a moderately strong intramolecular hydrogen bond from the imidazole N_1–H to the carbonyl oxygen. Complexation of both *E*- and *Z*-methyl urocanate with BF_3 occurs on the imidazole N_3 rather than carbonyl oxygen and causes a large blue-shift in their electronic absorption spectra. The free esters undergo reversible *E*,*Z* photoisomerization whereas their BF_3 complexes undergo one-way $E \rightarrow Z$ photoisomerization. The failure of the complexed (*Z*)-urocanate to photoisomerize is attributed to an increase in the intramolecular hydrogen bond strength upon complexation.

We have recently reported that irradiation of α,β-unsaturated esters in the presence of Lewis acids such as BF_3 or $EtAlCl_2$ can result in enhanced $E \rightarrow Z$ photoisomerization and inhibition of competing unimolecular photochemical processes.[1-3] For example, 313-nm irradiation of methyl (*E*)-cinnamate (*E*-**1**) in the absence or presence of 0.2 mol equiv of $EtAlCl_2$ results in optimum yields of 46% and 92% *Z*-**1**, respectively.[1,2] Enhanced $E \rightarrow Z$ isomerization results from selective excitation of the ground-state complex of the Lewis acid with the ester carbonyl oxygen.

We report here the results of our investigation of photoisomerization reactions of two heterocyclic analogues of methyl cinnamate, methyl furylacrylate (3-(2-furyl)propenoate, **2**), and methyl urocanate (3-(1-*H*-imidazol-4-yl)propenoate, **3**). The photoisomerization reactions of *E*-**3**[4,5] and of the parent acids of

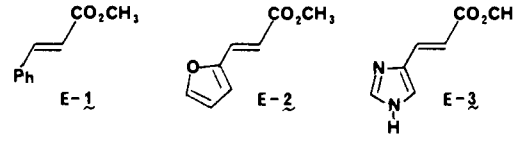

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Table I. Absorption Spectral Data for Esters and Lewis Acid Complexes[a]

ester	Lewis acid	λ_{max}	ϵ_{max}	$\epsilon_{h\nu}$[b]
E-**1**[c]	none	277	24 200	400
	BF_3	313	27 200	17 800
Z-**1**	none	267	10 600	500
	BF_3	303	12 000	11 500
E-**2**	none	300	24 000	20 000
	BF_3	348	20 200	14 700
	$BF_3{\cdot}OEt_2$	350 (sh)	7 500	4 700
	$EtAlCl_2$	356	23 200	21 600
Z-**2**	none	305	18 800	18 000
	$BF_3{\cdot}OEt_2$	350 (sh)	2 500	1 600
	$EtAlCl_2$	357	9 200	8 800
E-**3**	none	284	17 300	3 200 (5 600)[d]
	$BF_3{\cdot}OEt_2$	266	9 300	8 800[d]
	$EtAlCl_2$	274	15 900	10 700[d]
Z-**3**	none	308	17 700	17 300 (1 300)[d]
	$BF_3{\cdot}OEt_2$	274	22 200	12 700[d]

[a] Dichloromethane solutions of 5×10^{-5} M ester. [b] Irradiation wavelength = 313 nm except as noted. [c] Data from ref 1. [d] 254 nm.

E-**2**[6] and *E*-**3**[7] have previously been reported, the photochemistry of urocanic acid being of special interest due to its possible role in protecting the human epidermis from sunlight.[7] While the photochemical behavior of *E*- and *Z*-**2** and their Lewis acid complexes is in some respects similar to that of *E*- and *Z*-**1**, the behavior of *E*-**3** and *Z*-**3** is markedly different. These differences are attributed to the existence of an N—H···O=C internal hydrogen bond in the noncomplexed ester in *Z*-**3** and to Lewis acid complexation on the imidazole nitrogen rather than the carbonyl oxygen of *E*- and *Z*-**3**.

Results and Discussion

Spectroscopic Characterization of Ester and Lewis Acid Complexes. The *E* and *Z* isomers of esters **1**–**3** all display a single broad long wavelength absorption band between 267 and 308 nm (Table I). In the case of *E*-**1** this band is attributed to a π,π^* intramolecular charge transfer transition in which the HOMO is localized on the styryl portion of the molecule and the LUMO on the enone portion of the molecule.[8] The lower energy and higher intensity of the transition for *E*-**1** vs. *Z*-**1** is due to differences in planarity. Crystallographic data establish that (*E*)-cinnamic acids and their esters are essentially planar in the solid state[9] while comparisons of absorption spectra with calculations indicate that in the *Z* isomers the phenyl group is rotated out of the enone plane by ca. 45°.[10]

The absorption maxima of both *Z*-**2** and its parent acid[6] occur at lower energies than those of their *E* isomers (Figure 1). Fueno et al.[10b] have observed that for fully planar β-substituted styrenes such as cinnamonitrile, the excitation energy and oscillator strength of the *Z* isomer are lower than those of the *E* isomer. The smaller steric demand of the β-furyl vs. phenyl group is reflected in reduced bond angle deformations in the crystal structures of β-furylacryamide vs. *p*-chlorocinnanamide[11] and may result in a more planar structure for *Z*-**2** vs. *Z*-**1**. The lower excitation energies for both *E*- and *Z*-**2** vs. **1** plausibly reflect the lower ionization

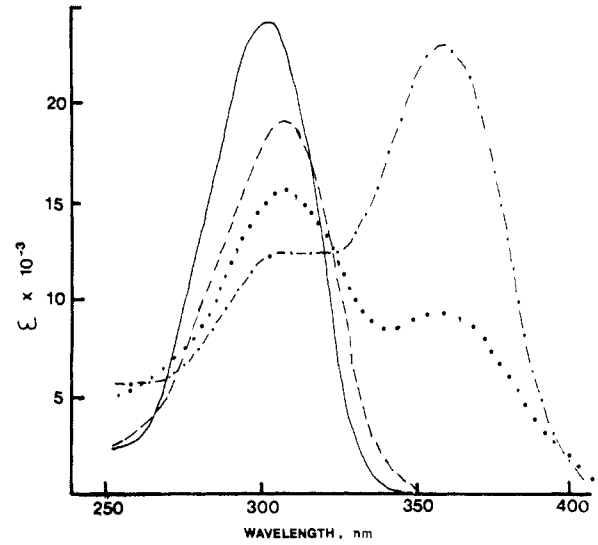


Figure 1. Absorption spectra of 5×10^{-5} M *E*-**2** in the absence (—) and presence (···) of $EtAlCl_2$ and *Z*-**2** in the absence (- - -) and presence (···) of $EtAlCl_2$ (2.0 molar equiv).

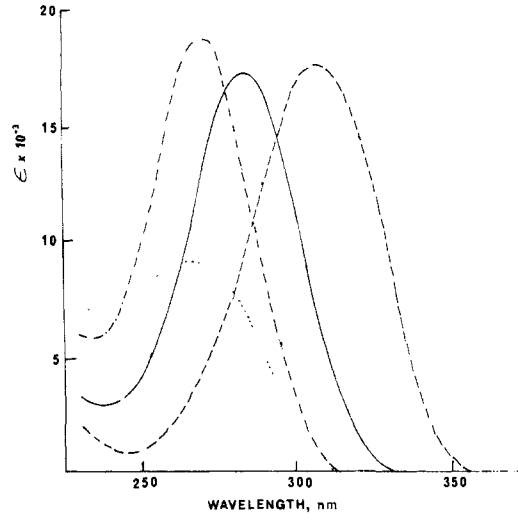
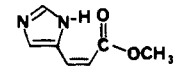


Figure 2. Absorption spectra of 6×10^{-5} M *E*-**3** in the absence of (—) and presence (···) of BF_3 and of *Z*-3 in the absence (- - -) and presence (···) of BF_3 (2.0 molar equiv $BF_3{\cdot}OEt_2$).

potential of furan vs. benzene,[12] which would raise the energy of the styryl-localized HOMO.

The absorption maximum of *Z*-**3** (but not its parent acid[7]) also occurs at lower energy than that of its *E* isomer (Figure 2). The difference in excitation energies for *E*-**3** vs. *Z*-**3** is larger than in the case of **2**, and the oscillator strengths of the *E* and *Z* isomers are more nearly equal. Valentine et al.[6] have recently investigated the infrared spectroscopy of *E*- and *Z*-**3** and find that *Z*-**3** exists exclusively as the N-**1**(H) tautomer in an intramolecularly hydrogen bonded s-cis conformation in methylene chloride or chloroform solution. In agreement with their conclusion that *Z*-**3** forms an intramolecular hydrogen bond but *E*-**3** does not, we find



s-cis Z-**3**

that the N–H proton of *E*-**3** is readily observed by ^1H NMR in CD_2Cl_2 solution, whereas the N–H proton of *Z*-**3** is broadened to the point that it is barely distinguishable (Table II).

Intramolecular hydrogen bonding could lower the excitation energy of *Z*-**3** vs. *E*-**3** either by increasing the planarity of the

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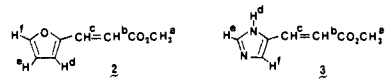
Table II. ^{1}H NMR Data for Esters and Lewis Acid Complexes



2 3

ester	chemical shift					
	H^a	H^b	H^c	H^d	H^e	H^f
E-**2**[a]	3.77	6.27	7.40	6.57	6.40	7.42
E-**2**:$EtAlCl_2$	4.13	6.60	7.90	6.97	6.53	7.60
$\Delta\delta$	0.36	0.33	0.50	0.40	0.13	0.18
Z-**2**[b]	3.77	5.66	6.75	7.62	6.43	7.40
Z-**2**:$EtAlCl_2$	4.30	6.02	7.17	7.15	6.60	7.63
$\Delta\delta$	0.57	0.36	0.42	−0.46	0.17	0.23
E-**3**[c]	3.65	6.40	7.60	9.17[e]	7.75	7.50
E-**3**:BF_3	3.80	6.80	7.80		9.20	8.30
$\Delta\delta$	0.15	0.40	0.20		1.45	0.80
Z-**3**[d]	3.75	5.70	6.80	9.53[e]	7.70	7.40
Z-**3**:BF_3	3.85	5.85	7.10		8.35	7.85
$\Delta\delta$	0.10	0.15	0.30		0.65	0.45

[a] J_{bc} = 15.6, J_{de} = 3.5, J_{ef} = 2.0 Hz (CD_2Cl_2). [b] J_{bc} = 12.1, J_{de} = 3.6, J_{ef} = 1.8 Hz (CD_2Cl_2). [c] J_{bc} = 15.8 Hz ($(CD_3)_2C{=}O$). [d] J_{bc} = 12.7 Hz ($(CD_3)_2C{=}O$). [e] CD_2Cl_2 solution.

Table III. Thermal Isomerization Data

ester	% $E_{110°}$	$K_{110°}$	ΔG, kcal/mol
1	99.9 ± 0.1	1,000	5.2
2	94.4 ± 0.1	170	3.9
3	33.0 ± 0.2	0.49	−0.53

extended chromophore or by perturbing its electronic structure. The tautomeric diazafulvadieneol would be expected to have a substantially lower singlet energy than a conjugated ester; however, the highly similar ^{1}H NMR data for the methoxy and vinyl protons of *Z*-**2** and *Z*-**3** (Table II) would appear to rule out extensive changes in the electron density of *Z*-**3** due to intramolecular hydrogen bonding. The parent urocanic acids absorb at shorter wavelength in aqueous solution at pH 7.40 than do *E*- and *Z*-**3**, and the excitation energy of the *Z* isomer is greater than that of the *E* isomer.[7] The higher excitation energy for the zwitterionic acid may result from protonation of the imidazole which would raise the energy of the styryl-localized HOMO.

In order to obtain further information about the relative stabilities of the *E* vs. *Z* isomers for **1**–**3**, the acid catalyzed thermal isomerization of these esters was investigated. Equilibrium constants obtained in refluxing toluene with catalytic amounts of *p*-toluenesulfonic acid and values of ΔG for $Z \rightarrow E$ isomerization are given in Table III. On the assumption that the *E* isomers are all planar and strain free, the magnitude of ΔG is determined by nonbonded repulsion between the ester and aromatic groups in the *Z* isomers. The 1.4-kcal/mol difference in ΔG values for *E*-**2** vs. *E*-**1** plausibly reflects the smaller steric requirements of the furan vs. benzene ring.[11] Since the steric requirements for furan and imidazole rings should be similar, the 4.4-kcal/mol difference in ΔG values for **3** vs. **2** is assumed to reflect the strength of the intramolecular hydrogen bond in *Z*-**3**.

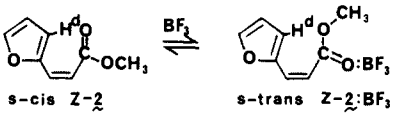
Addition of the strong Lewis acids BF_3 or $EtAlCl_2$ to solutions of esters **2** and **3** causes marked changes in their spectroscopic properties as previously reported for **1** (Table I).[1,13] Saturation of a solution of *E*-**2** with BF_3 gas results in the disappearance of the 300-nm maximum and the appearance of a band at 348 nm attributed to the BF_3 complex of *E*-**2**. The red shift observed upon BF_3 complexation corresponds to an energy difference of 13.3 kcal, somewhat larger than the value for *E*-**1** (11.9 kcal).[1] Addition of 2.0 molar equiv of BF_3·OEt_2 to solutions of *E*- and *Z*-**2** causes a reduction in intensity of the 300-nm bands and the appearance of shoulders at ca. 350 nm. Similarly, addition of 2 molar equiv of $EtAlCl_2$ to solutions of *E*- and *Z*-**2** causes reduction in intensity of the 300-nm bands and the appearance of bands at 356 and 357 nm, respectively (Figure 1). Evidently, complete complexation does not occur with 2.0 molar equiv of BF_3·OEt_2 or $EtAlCl_2$.

Addition of BF_3·OEt_2 or $EtAlCl_2$ to dichloromethane solutions of *E*- or *Z*-**3** results in the disappearance of their long wavelength band and the appearance of bands at shorter wavelengths (Figure 2) attributed to the Lewis acid complex. The use of 2.0 molar equiv of BF_3·OEt_2 is sufficient to effect complete conversion of the spectra of the free esters to those of their BF_3 complexes. Thus *E*- and *Z*-**3** form stronger BF_3 complexes than do **1** or **2**. The excitation energy of the BF_3 complex of *Z*-**3** is lower than that for *E*-**3** while its oscillator strength is greater.

The different effect of Lewis acid complexation upon the absorption spectra of the urocanic esters *E*- and *Z*-**3** vs. **1** and **2** and other α,β-unsaturated esters[1-3] is attributed to complexation on the more basic imidazole nitrogen vs. less basic carbonyl oxygen. Complexation, like protonation of a nonbonding nitrogen orbital, should lower the energy of the styryl-localized HOMO leading to an increase in the excitation energy, whereas complexation of oxygen should lower the energy of the enone-localized LUMO leading to a decrease in excitation energy.

Conclusive evidence for complexation of *Z*-**3** on the imidazole nitrogen is provided by the effect of BF_3 on the infrared spectrum. As previously reported by Valentine et al.,[6] the N–H stretches of *E*- and *Z*-**3** in dilute chloroform solution occur at 3465 and 3280 cm^{-1}, respectively. Addition of 2.0 molar equiv of BF_3·OEt_2 to an 0.06 M dichloromethane solution of *Z*-**3** effects a change in the N–H stretching frequency from 3270 to 3150 cm^{-1} but no change in the C=O stretch (1698 cm^{-1}). In contrast, addition of BF_3 to *E*-**1** effects a change in the C=O stretch from 1715 to 1647 cm^{-1}. The change in the N–H stretching frequency is similar to that reported for complexation of *Z*-**3** with iron(III) tetraphenylporphyrin[6] and is indicative of significantly stronger intramolecular hydrogen bonding for complexes vs. noncomplexed *Z*-**3**. Both inter- and intramolecular hydrogen bond strengths are enhanced upon complexation of imidazole. An increase in the imidazole dimer hydrogen bond strength of 38 kcal/mol has recently reported for complexation with Zn^{2+}.[14]

Further information about the Lewis acid complexes of **2** and **3** is provided by their ^{1}H NMR spectra. Spectral data for the free and complexed esters are summarized in Table II. The assignments of *E*- and *Z*-**2** are in agreement with published results.[15] The spectrum of uncomplexed *Z*-**2** is notable for the exceptionally large H^d chemical shift which we attribute to proximity of H^d to the carbonyl group in the s-cis conformation. Addition of 1.0 molar equiv of $EtAlCl_2$ to CD_2Cl_2 solutions of *E*- or *Z*-**2** results in downfield shifts for all of the ^{1}H signals (except for that of H^d of the *Z* isomer) but only minor changes in coupling constants, as previously observed for *E*- and *Z*-**1**.[1,2] The upfield shift observed for H^d of *Z*-**2** plausibly results from a change in molecular conformation from s-cis to s-trans upon complexation (eq 1), as observed crystallographically for *E*-**1** and its $SnCl_4$



s-cis *Z*-**2** s-trans *Z*-**2**:BF_3 (1)

complex.[16] Addition of >1.0 molar equiv of $EtAlCl_2$ causes no further change in chemical shifts, indicative of the formation of a 1:1 complex. Addition of 1.0 molar equiv of BF_3·OEt_2 results in much smaller downfield shifts than those obtained with $EtAlCl_2$, which reflect the time averaged spectra of free and complexed esters.

The ratio of equilibrium constants for complexation of *E*-**2** vs. *Z*-**2** can be obtained as previously described by Fratiello and

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Table IV. Photostationary States and Quantum Yields for Photoisomerization[a]

ester	Lewis acid	λ_{ex}, nm	$\Phi_{E,Z}$	% Z_{obsd}[b]	% Z_{calcd}[c]
E-**1**[d]	none	313	0.30	46	46
	BF_3·OEt_2	313	0.70	88	93
Z-**1**	none	313	0.29		
	BF_3·OEt_2	313	0.28		
E-**2**	none	313	0.50	52	55
	BF_3·OEt_2	365	0.69	94	94
	$EtAlCl_2$	365		92	
Z-**2**	none	313	0.45		
	BF_3·OEt_2	365	0.33		
E-**3**	none	254		85	
	none	313	0.63	16	26
	BF_3·OEt_2	254		>95	
Z-**3**	none	313	0.33		

[a] Dichloromethane solutions of 0.02 M ester. [b] Optimum conversion of *E* to *Z* isomers. [c] Conversion of *E* to *Z* isomers calculated with eq 4. [d] Data from ref 1.

Schuster.[17] Comparison of the $\Delta\delta$ values in Table III with $\Delta\delta^{obsd}$ values obtained from an equimolar mixture of *E*-**2** and *Z*-**2** with 0.5 molar equiv of $EtAlCl_2$ with use of eq 2 provides a value of $K_E/K_Z = 3.3 \pm 0.2$. Similar values have been reported for Lewis acid complexes of cinnamic esters.[1,2]

$$K_E/K_Z = \frac{\Delta\delta_E{}^{obsd}/\Delta\delta_E}{\Delta\delta_Z{}^{obsd}/\Delta\delta_Z} \qquad (2)$$

The ^1H NMR spectra of *E*- and *Z*-**3** have recently been assigned by Kinoto et a.[4] by analogy to those for the isomeric urocanic acids. We have reversed their assignments for the imidazole protons H^e and H^f on the basis of ample precedent for larger chemical shifts for H_2 vs. H_4 or H_5 in neutral substituted imidazoles.[18] Since neutral urocanic acids exist in the zwitterionic form,[7] protonation of the imidazole ring will result in substantial differences in the spectra of the esters vs. free acids. The most interesting feature of the ^1H NMR spectra of the urocanic esters is the previously mentioned appearance of the N–H protons. The N–H proton of *E*-**3** is slightly broadened, while the N–H proton of *Z*-**3** is significantly broadened in CD_2Cl_2 solution due to intramolecular hydrogen bonding. Neither N–H proton can be detected in $(CD_3)_2C{=}O$ or CD_3OD[4] solution due to rapid exchange.

Addition of BF_3·OEt_2 to CD_2Cl_2 or $(CD_3)_2CO$ solutions of *E*- or *Z*-**3** results in downfield shifts for all of the ^1H NMR signals (Table II). Addition of 2.0 molar equiv is sufficient to quantitatively convert *E*- and *Z*-**3** to their BF_3 complexes. Use of 0.5 molar equiv results in substantial line broadening. This reflects slow exchange between free and complexed esters and is indicative of stronger complex formation between BF_3 an **3** vs. **2** or **1**. Complextion results in $\Delta\delta$ values which decrease in the order imidazole > vinyl > methoxyl in accord with complexation on the imidazole nitrogen. The larger $\Delta\delta$ value for H^e vs. H^f is consistent with our assignment of these protons.

Photoisomerization Reactions. Irradiation of the *E* or *Z* isomers of **1**–**3** (0.02 M) in dichloromethane solution with 313-nm light results in the formation of photostationary states containing 46, 52, and 16% *Z* isomer, respectively (Table IV). Irradiation of *E*- or *Z*-**3** with 254-nm light results in the formation of a photostationary state containing 85% *Z*-**3**. Photodimerization does not compete with photoisomerization under these conditions. The different photostationary states obtained for **1**–**3** primarily reflect differences in the absorption spectra of their *E* and *Z* isomers (Figures 1 and 2; Table I). The red-shifted absorption of *Z*-**3** allows moderately selective excitation of the *Z* isomer at 313 nm and the *E* isomer at 254 nm.

Photostationary states for *E*,*Z* isomerization can be calculated by using eq 3, in cases where the extinction coefficients and

$$\frac{[Z]}{[E]} = \frac{\Phi_E}{\Phi_Z}\frac{\epsilon_E}{\epsilon_Z} \qquad (3)$$

isomerization quantum yields are known. Quantum yields for *E* → *Z* (Φ_E) and *Z* → *E* (Φ_Z) isomerization of **1**–**3** using 313-nm light are summarized in Table IV. The calculated photostationary states for **1** and **2** are in good agreement with the measured values (Table IV), while the calculated value is larger than the measured value for **3**.

The sum of the isomerization quantum yields $\Phi_E + \Phi_Z = 0.95$ and 0.99 for **2** and **3**, respectively. On the assumption that isomerization occurs via a common twisted intermediate,[19] nonradiative decay does not compete as effectively with isomerization for these esters as it does for **1**.[1] In the case of **3**, this indicates that intramolecular hydrogen bonding does not inhibit isomerization of electronically excited *Z*-**3**. Electronic excitation is known to increase the N–H acidity of nitrogen containing heterocyclic molecules.[20] This might result in weakening of the intramolecular hydrogen bond in the excited vs. ground states.

Irradiation of the parent acids of **1**–**3** at 254 nm is reported to yield photostationary states containing 53%,[10a] 20%,[6] and 42%[7] *Z* isomer, respectively. The difference in photostationary states obtained with esters vs. acids reflects differences in their absorption spectra or quantum yields. Morrison et al.[7] have reported that the photostationary states and isomerization quantum yields for (*E*)- and (*Z*)-urocanic acid are dependent upon excitation wavelength. The photostationary state content of the *Z* isomer increases with increasing excitation wavelength, reflecting primarily an increase in the ratio ϵ_E/ϵ_Z. The sum of the quantum yields for 313-nm excitation is 0.99, the same as observed for the esters *E*- and *Z*-**3**, whereas 254-nm excitation results in highly inefficient isomerization ($\Phi_Z + \Phi_Z = 0.13$). As in the case for cinnamic acids and esters,[1] the broad absorption bands of **2** and **3** may represent several electronic transitions to excited states with different photophysical and photochemical properties.

Irradiation of *E*- or *Z*-**2** in the presence of the Lewis acids BF_3·OEt_2 or $EtAlCl_2$ results in enhanced *E* → *Z* conversions, as is the case for **1** (Table IV). The use of 365-nm irradiation allows selective excitation of complexed vs. noncomplexed esters (Figure 1) and results in 94% conversion of *E*-**2** to *Z*-**2** with use of 0.25–1.5 molar equiv of BF_3·OEt_2 and 92% conversion with use of 0.1–0.5 molar equiv of $EtAlCl_2$. Use of higher concentrations of $EtAlCl_2$ results in lower conversions of *E*-**2** to *Z*-**2**. Quantum yields for isomerization of *E*-**2** and *Z*-**2** (Φ_{EA} and Φ_{ZA}) in the presence of 0.25 molar equiv of BF_3·OEt_2 with use of 365-nm light are 0.69 and 0.33, respectively. Both values decrease slightly with increasing BF_3·OEt_2 concentration, with values of 0.64 and 0.27, respectively, being obtained with use of 2.0 molar equiv of BF_3·OEt_2. The use of 0.25 molar equiv of BF_3·OEt_2 is sufficient to provide complete absorption of 365-nm light by the ester:BF_3 complexes.

We have observed that the photostationary state for isomerization of incompletely complexed cinnamic esters can be described by eq 4.[1]

$$\frac{[Z]}{[E]} = \frac{\Phi_{EA}}{\Phi_{ZA}}\frac{\epsilon_{EA}}{\epsilon_{ZA}}\frac{K_{EA}}{K_{ZA}} \qquad (4)$$

The ratio of equilibrium constants K_{EA}/K_{ZA} obtained from ^1H NMR data for *E*- and *Z*-**2** with $EtAlCl_2$ is 3.3 ± 0.2. Assuming a similar ratio for BF_3, the photostationary state calculated for isomerization of *E*- and *Z*-**2** in the presence of 0.25 molar equiv of BF_3·OEt_2 is the same as the observed photostationary state (94% *Z*-**2**). While the precise agreement of observed and calculated values is fortuitous, it does confirm the utility of eq 4 in analyzing the photostationary states obtained for Lewis acid complexes of α,β-unsaturated esters.

Lewis acid complexation of *E*- and *Z*-**3** causes a blue-shift in their absorption spectra (Figure 2). Since their complexes do not

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absorb appreciably at 313 nm, photoisomerization with 254-nm light was investigated. Irradiation of *E*-**3** with 1.0 molar equiv of BF_3·OEt_2 results in >95% conversion to *Z*-**3** by ^1H NMR and GC analysis. Since both *E*- and *Z*-**3** are fully complexed, the photostationary state will be described by eq 3. Moreover, as the BF_3 complex of *Z*-**3** absorbs more strongly at 254 nm than that of E-$_3$, it is evident that $\bar{\Phi}_{EA} \gg \Phi_{ZA}$. A possible explanation for the observation of reversible photoisomerization of noncomplexed *E*- or *Z*-**3** but irreversible $E \rightarrow Z$ isomerization for their BF_3 complexes is provided by the observation of significantly enhanced intramolecular hydrogen bond strength for *Z*-3 upon complexation with BF_3. Increased intramolecular hydrogen bond strength might result in a large thermal barrier for isomerization on the excited state energy surface and thus preclude $Z \rightarrow E$ photoisomerization.

Concluding Remarks. Irradiation of both β-furylacrylic (365 nm) and urocanic acids (254 nm) in the presence of Lewis acids results in nearly quantitative $E \rightarrow Z$ photoisomerization, thereby extending the scope of Lewis acid catalyzed photoisomerization to heterocyclic analogues of cinnamic esters.[1-3] While the effect of Lewis acids on the photoisomerization equilibria of these esters is similar, the mechanistic bases differ significantly. Lewis acid complexation of *E*- or *Z*-**2** occurs on the carbonyl oxygen causing a large red-shift in the absorption spectrum, whereas complexation of *E*- or *Z*-**3** occurs on the imidazole N_3 causing a large blue-shift in the absorption spectrum. Selective $E \rightarrow Z$ photoisomerization of **2** results from a combination of three factors: stronger *E* vs. *Z* complexation, stronger absorption of light by the *E* vs. *Z* complex, and a higher quantum yield for $E \rightarrow Z$ vs. $Z \rightarrow E$ photoisomerization. Selective isomerization of **3** is solely a consequence of the photostability of *Z*-**3**. These results serve to illustrate the importance of the site of complexation in determining the spectroscopic properties and photochemical behavior of Lewis acid complexes.

Experimental Section

General Methods. NMR spectra were obtained on a Varian CFT20 or a Varian EM390 spectrometer. Ultraviolet absorption spectra were recorded on a GCA/McPherson EU 700 spectrophotometer, infrared spectra on a Perkin-Elmer 283 spectrophotometer, and mass spectra on a Hewlett-Packard 5986 GC/MS. Irradiated solutions were analyzed on a Hewlett-Packard 5750 or Varian 3700 flame ionization gas chromatograph with a calibrated 6 ft × $^1/_8$ in. column containing 5% SF-96 on Chromosorb G (*E*,*Z*-**2**) or 3% SP 2100 on Supelcoport (*E*,*Z*-**3**).

Irradiations were conducted with a Rayonet reactor with 254-nm lamps or a Hanovia 450 W medium pressure mercury lamp in a water-cooled Pyrex lamp well. Corning glass filters 7-54 and 0-52 were used to isolate 365-nm light, and monochromatic 313-nm irradiation was obtained with use of a potassium chromate filter solution with the Hanovia lamp. Quantum yield and conversion vs. time measurements were carried out on a merry-go-round apparatus with use of potassium ferrioxalate (254 nm), *trans*-stilbene[21] (313 nm), or Amberchrome 540[22] (365 nm) solution actinometers run in triplicate. Solutions of ester in dichloromethane contained in 13 mm o.d. quartz or Pyrex test tubes equipped with serum caps were bubbled with dry N_2. Lewis acid solutions were added by syringe under a N_2 atmosphere in a Kewaunee Scientific Products drybox.

Acid catalyzed isomerization reactions were conducted by refluxing toluene solutions of 3.3×10^{-4} M *E*-**1**-**3** and *p*-toluenesulfonic acid. Solutions were monitored by GC until equilibrium was established.

Materials. Dichloromethane (Aldrich gold label) was distilled from phosphorus pentoxide, refluxed over calcium hydride, and distilled immediately by prior to use. (*E*)-β-Furylacrylic acid (Aldrich) was esterified via the acid chloride and distilled under reduced pressure (92-95 °C, 5 Torr). UV, Table I; ^1H NMR, Table II. (*E*)-Urocanic acid (Aldrich) was esterified by refluxing its hydrochloride salt in methanol. The hydrochloride salt of the ester was liberated as a colorless oil prior to use. UV, Table I; ^1H NMR, Table II.

Methyl (*Z*)-β-Furylacrylate (*Z*-2). Methyl (*E*)-β-furylacrylate (0.91 g, 6.0×10^{-3} mol) and BF_3·OEt_2 (300 mL, 0.36 g, 0.0026 mol) were dissolved in 0.2 L of dichloromethane under a dry nitrogen atmosphere. The solution was transferred to a Pyrex annulus, sealed with a septum, and irradiated for 3 h in a Rayonet reactor with broad-band 350-nm light. The solution was extracted with water, dried over magnesium sulfate, concentrated, and subjected to flash vacuum chromatography on silica gel (200 g) with 1% ethyl acetate/hexane. Pure *Z*-**2** (0.77 g, 85%) was obtained free of *E*-**2**. UV, Table I; ^1H NMR, Table II.

Methyl (*Z*)-Urocanate (*Z*-3). Methyl (*E*)-urocanate (0.3 g, 2.0×10^{-3} mol) and BF_3·OEt_2 (1.0 molar equiv) in 0.1 L of dichloromethane were irradiated under dry N_2 in a Vycor reaction flask with 254-nm light. The solution was extracted with water, dried over magnesium sulfate, concentrated, and subjected to evaporation distillation (110 °C, 1 Torr) to yield *Z*-**3** as a viscous, colorless oil (0.19 g, 63%). UV, Table I; ^1H NMR, Table II.

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Mechanism of OH Radical Reactions with Thymine and Uracil Derivatives†

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Abstract: Yields of reducing, 6-yl, oxidizing, 5-yl, and substituted methyl radicals, generated by OH radical reaction with uracil (U), thymine (T), and 1-methyluracil (1-MeU), were determined by pulse radiolysis in aqueous solutions at pH 7. The absolute yields and ratio of 5-yl/6-yl radicals in uracil (20% 5-yl-U, 80% 6-yl-U) are altered in methyl-substituted derivatives of uracil. For thymine one finds 35% of 5-yl-T and 57% of 6-yl-T and for 1-methyluracil 20% of 5-yl-1-MeU and 65% of 6-yl-1-MeU radicals. The yields of pyrimidine glycols in the presence of an oxidizing agent (G = 3.2 for thymine glycols, 4.3 for uracil glycols, 3.7 for 1-methyluracil glycol), as measured by HPLC, were shown to be equal to the yields of 5-OH-6-yl-Py reducing radicals of thymine (56% OH), uracil (80% OH), and 1-methyluracil (65% OH). It is suggested that 5-OH-6-yl radicals are the exclusive precursors of glycols. Mechanisms of glycol formation in the presence and absence of oxidizing agents are proposed and discussed.

Measurement of thymine glycol (5,6-dihydroxythymine), $T(OH)_2$, in urine has been suggested as a dosimeter of oxidative damage of DNA in humans and animals.[1] The suggestion is based on the rather high yield of $T(OH)_2$ (as thymine glycol and thymidine glycol) in human urine (32 nmol/day) and the 15 times

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